



Short communication

Carbon nanotube/ polypyrrole nanofibers core–shell composites decorated with titanium dioxide nanoparticles for supercapacitor electrodes

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HIGHLIGHTS

- We have explored interaction of carbon nanotubes and nanofibers of polypyrrole.
- Resulting powder is characterized by superior electrochemical response.
- Titanium dioxide/carbon nanotube complex improves the capacitance of powder.

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ABSTRACT

The development of new materials for hybrid supercapacitors requires the adequate combination of pseudocapacitance and electrical double layer capacitance, morphology, high surface area and low mass density of electrodes. In this work, we have explored a simple and low cost composite based on incorporation of titanium dioxide/single walled carbon nanotube complex during polymerization of hollow nanotubes of polypyrrole. The resulting composite is characterized by superior electrical properties (high conductivity) and improved electrochemical response. The optimization in the relative concentration of components of ternary composite results in a capacitance of 282 Fg^{−1} and specific energy density in order of 1.0 Wh kg^{−1} which is a result of synergistic interaction of components during polymerization of polymeric hollow nanotubes and core/shell structures of SWCNTs/polypyrrole decorated with titanium dioxide nanoparticles.

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1. Introduction

The increasing demand for clean energy sources applied in hybrid vehicles and electronic devices requires the development of new materials with superior electrochemical properties in comparison with conventional sources (such as hydrogen fuel cells, battery and capacitors) [1–4]. High energy level and low power density is a typical response of fuel cell while high power density and low energy density is a typical behavior of capacitors. In order to circumvent both limitations, an interesting application is based on production of materials with intermediate properties relative to fuel cells and capacitors, associated with low cost of production, long life cycle and fast charge rate.

Supercapacitors are electrochemical devices characterized by reasonable energy density (if compared with conventional batteries) with charging-discharging mechanisms dominated by pseudocapacitance and electrical double layer capacitance (EDLC) which is established by non-Faradaic process at electrolyte/electrode interface (carbon derivatives are potential candidates for application as EDLC electrodes) [5–8]. Charge storage processes in pseudocapacitors (conducting polymers and metal oxide particles) are dominated by typical Faradaic processes (fast redox reactions) [5].

Polypyrrole, polyaniline and polythiophene have been considered potential candidates for use in supercapacitors due to their high level of conductivity, good electrochemical properties and high flexibility. Polypyrrole (PPy) introduces additional advantages relative to the environmental stability and as a consequence it has been progressively applied as a conducting support with improved electrochemical response.

The application of polypyrrole nanotubes as template for supercapacitor electrodes introduces unique properties such as

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high conductivity, superior redox behavior [7] and high surface area. According ref. [9], specific surface area of polypyrrole nanotubes is $6.7\times$ higher than surface area of bulk polypyrrole.

Titanium dioxide has been explored as support for supercapacitor electrodes due to their superior electrical (semi-conducting) properties, high surface area and environmental stability [6]. Nanocarbon materials introduce additional advantages due to their high surface area, high conductivity and low mass density [5]. The incorporation of metal oxide particles in carbon derivatives has been progressively reported in the literature due to the strong interaction between materials such as carbon nanotubes and titanium dioxide nanoparticles which improves spatial confinement of TiO_2 and provides high surface area combined with faster redox reactions [10].

In order to maximize the energy density of organic composites based on conducting polymers, we have explored in a previous work [11] the production of supercapacitors from combination of EDLC (modified graphene oxide sheets) and pseudocapacitors (polypyrrole). The synergistic interaction between components and maximization in the surface area were the key to providing superior performance for supercapacitors.

In this work, we have explored an alternative system obtained from interaction of titanium dioxide particles/single walled carbon nanotubes complex with a matrix of hollow polypyrrole nanotubes and core/shell structures of SWCNT/decorated polypyrrole tubes. Tubular structures of polypyrrole are obtained from polymerization of pyrrole on the surface of methyl orange templates [12] and the interaction with carbon nanotubes contributes with production of core-shell structures of CNT/polypyrrole systems. The incorporation of complexes of titanium dioxide particles and carbon nanotubes into polymeric matrix represents an important step for optimization of electrical response of composite, surface area and electrochemical response of device due to the association of EDLC and pseudocapacitor effects.

2. Experimental

Pyrrole (Aldrich) was distilled before the use. Methyl orange (Vetec), ferric chloride (Vetec), single walled carbon nanotubes (0.7–1.3 nm diameter – Aldrich), sodium dodecyl sulfate (Aldrich) and titanium dioxide (diameter < 25 nm and purity of 99.7%, Aldrich) were used as received.

The morphology of composites was analyzed by a scanning electron microscopy (SEM Vega 3XMU/EDS) with an accelerating voltage of 5 kV. The structure of material was characterized by analysis of FTIR (KBr method) using a IR Prestige-21 Fourier transform infrared spectrometer Shimadzu. Electrical impedance measurements were performed using an impedance/gain phase analyzer (Solartron SI 1260 + dielectric interface 1296). Electrochemical response of polymeric electrodes was characterized by cyclic voltammetry (CV) while galvanostatic charge/discharge (GCD) measurements were performed using a 2-electrode configuration in which both electrodes are impregnated with electrolyte (KCl – 1M) and separated by a porous Celgard. Electrical contacts are established by disposition of device between two metallic parallel plates (sample holder Solartron 12962). The potential range for cyclic voltammetry varied from -0.3 V to 0.3 V and a Potentiostat/Galvanostat Metrohm Autolab AUT302N was used in order to perform the electrochemical characterization of resulting devices.

2.1. Synthesis of polypyrrole nanotubes

The synthesis of polypyrrole hollow nanotubes was established according procedure reported by X. Yang et al. [8,9]. The first step

is established with complete dispersion of 0.1 g of methyl orange in 60 mL Millipore water. Under intense stirring (300 rpm) and immersed in an ice bath, 0.486 g of ferric chloride is dispersed at aqueous solution of methyl orange with posterior inclusion of 0.21 mL of pyrrole. The mixture acquires a blackish aspect with high viscosity and is maintained under stirring (at dark condition) during 24 h. The resulting powder is washed with ethanol and water (for methyl orange elimination) several times and dried under vacuum. Residual water is eliminated in an oven (at 60°C) during 1 h.

2.2. Preparation of complexes of TiO_2 /SWCNT

Complexes of TiO_2 /SWCNT were prepared according procedure established by Dechakiatkrai et al. [13]. 50 mg of TiO_2 , 0.4 mg of SWCNT and 0.4 mg of SDS were mixed in 10 mL of ethanol and sonicated during 1 h. After 5 min of centrifugation at 10,000 rpm, the resulting material was dried at 70°C during 1 h. The resulting powder is stored under dark condition.

2.3. Synthesis of TiO_2 /SWCNT/PPy supercapacitors

After the dispersion of 0.1 g of methyl orange in 60 mL of Millipore water, variable amount of additive (TiO_2 , SWCNT or TiO_2 /SWCNT complex), as described in Table 1, is dispersed in solution and sonicated during 5 min. Posterior steps of synthesis remain the same as previously described for preparation of polypyrrole nanotubes.

Disc-shaped pellets with 1.2 cm of diameter are obtained from compression (5 kN) of powder and are prewetted in an electrolyte (KCl – 1 M, during 24 h) before the use as symmetric electrodes in a symmetrical two electrodes configuration (separation established by a Celgard membrane impregnated in the same electrolyte). CV and GCD techniques are explored in order to describe the capacitive behavior of resulting composite. In an ideal CV curve of EDLC device, a squared shape curve is expected and increase in the area is proportional to the increase of capacitance, allowing the direct comparison of different CV curves and the resulting capacitance. On the other side, GCD curves return important information about the specific capacitance of device, measured during the discharge of device and calculated using the relation: $C_{sp} = 4I/(m(dV/dt))$ where dV/dt represents the slope of discharge charge, m the total mass of electrodes and I the constant current during discharge [14]. Specific energy density (E_{sp}) is calculated from GCD curves using the relation $E_{sp} = \Delta E_{it}/m$; where $\Delta E = (E_{max} + E_{min})/2$, E_{max} and E_{min} are the potential at the beginning and end of discharge curve, I is the applied current established during discharge, m the total mass of electrodes and t is the discharge time [2].

3. Results and discussion

The morphology of resulting device - PPy/ TiO_2 /SWCNT (sample C_1) is characterized by homogeneous dispersion of nanotubes of

Table 1
Relative composition of samples applied as electrodes for supercapacitors.

Sample	Pyrrole (mL)	TiO_2 (mg)	TiO_2 /SWCNT complex (mg)	SWCNT (mg)
T_0	0.21	0	0	0
T_1	0.21	4.8	0	0
T_2	0.21	9.6	0	0
C_1	0.21	0	4.8	0
C_2	0.21	0	14.4	0
S_1	0.21	0	0	0.4

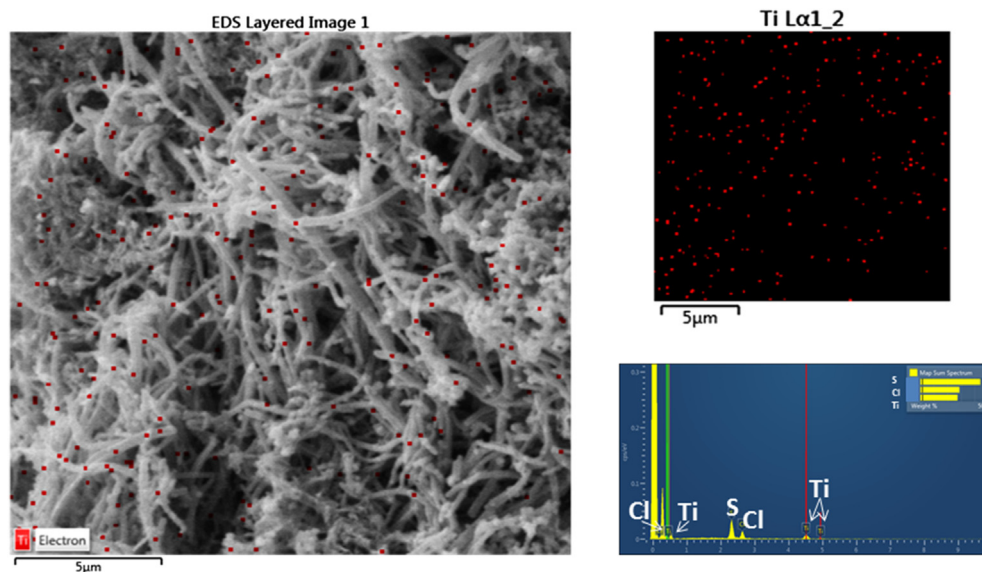


Fig. 1. SEM image (7000 \times magnification) of sample C_1 overlaid with EDS data – (red dots indicate the distribution of TiO_2 on surface of composite). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

polypyrrole/single walled carbon nanotubes, as shown in Fig. 1. Overlaid EDS on image indicates a reasonable homogeneity of dispersion of TiO_2 particles (red dots) (in web version) on polymeric matrix. FTIR spectrum of samples (Fig. 2) is characterized by peaks at 1546 cm^{-1} , 1162 cm^{-1} , 1026 cm^{-1} and 964 cm^{-1} which can be assigned to C=C stretching vibration, C–N stretching vibrations, N–H out-of-plane vibrations and C–H out-of-plane vibrations, respectively, in agreement with typical signature of specific groups of polypyrrole [1,15,16]. These peaks are present in different composites (PPy/ TiO_2 – Sample T_2 , PPy/SWCNT – Sample S_1 and PPy/ TiO_2 /SWCNT – Sample C_2), in an indication that reasonable degree of polymerization is established in the presence of additives (TiO_2 or TiO_2 /SWCNT complex).

The electrical impedance of composites pellets was analyzed as a function of composition and frequency. We have measured the response of material in the absence of electrolyte in order to

identify the electrical transport level of polymeric matrix. The results (see Fig. 3) indicate that superior electrical properties (lower impedance) are obtained from incorporation of titanium dioxide particles, single walled carbon nanotubes and TiO_2 /SWCNT complex into polymeric template (samples T_2 , S_1 , and C_2 , respectively). The introduction of TiO_2 /SWCNT complex reduces the level of impedance of composite which is a result of strong interaction of particles and nanotubes during synthesis of polymeric nanotubes.

In spite of characteristic low electrical conductivity of metal oxide particles, an interesting aspect to be observed is related with synergistic interaction of components which results in the production of materials with higher conductance than neat components. The influence of titanium dioxide on electrochemical response was analyzed at different concentration with the aim of optimizing the electrochemical performance of device. As we can see in Fig. 4, the required time for five complete charge–discharge

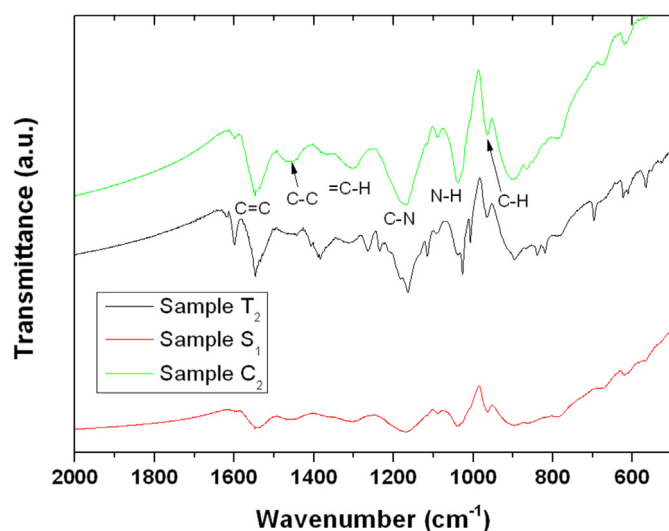


Fig. 2. FTIR spectra of PPy/SWCNT (sample S_1), PPy/ TiO_2 (sample T_2), PPy/ TiO_2 /SWCNT (sample C_2).

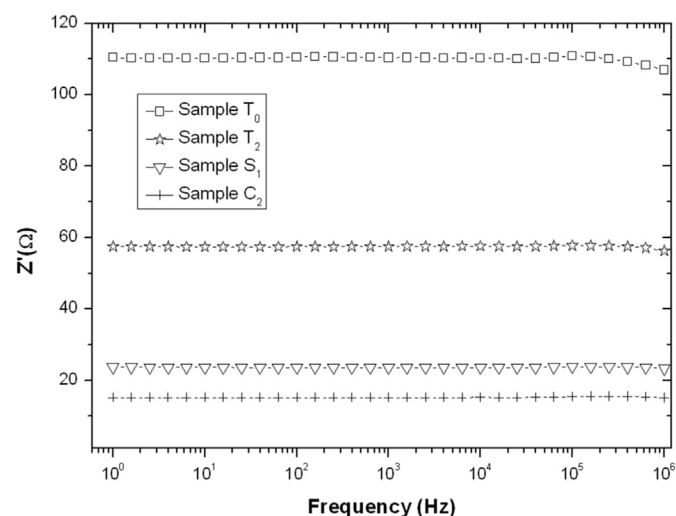


Fig. 3. Spectrum of real part of impedance of pellets of polypyrrole, polypyrrole/ TiO_2 , polypyrrole/SWCNT and polypyrrole/ TiO_2 /SWCNT complexes (samples T_0 , T_2 , S_1 and C_2).

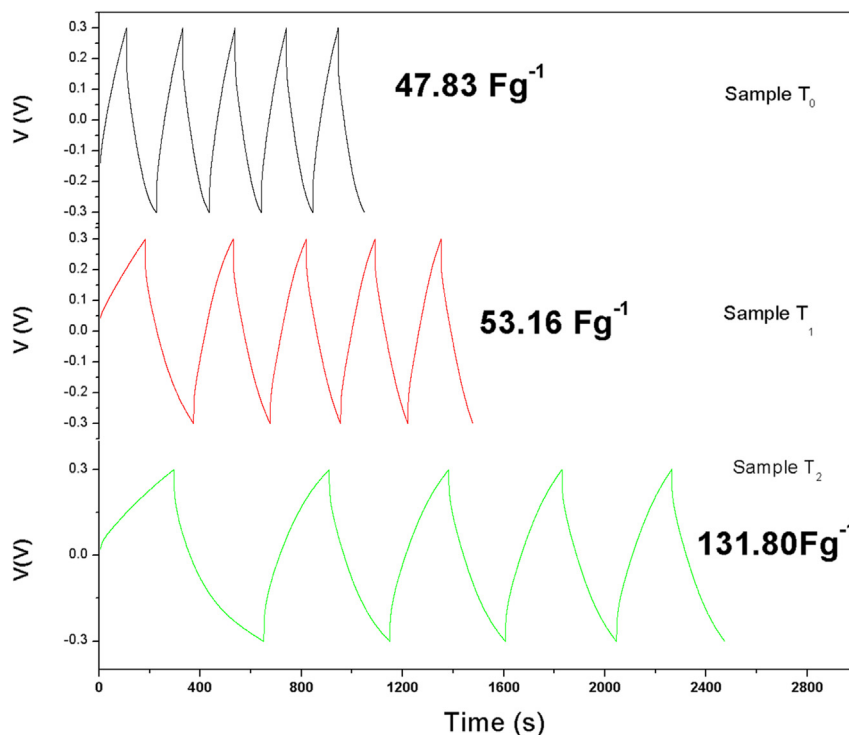


Fig. 4. GCD curves of composites at different relative concentration of TiO_2/PPy (samples T_0 , T_1 and T_2).

(CD) curves at constant current (5 mA – charge/–5 mA – discharge) depends on the amount of titanium dioxide disposed in the matrix during polymerization, as a result of strong dependence of composite with concentration of titanium dioxide. In the absence of titanium dioxide (neat polypyrrole) the capacitance (calculated from GCD curves) is in order of 47.8 Fg^{-1} (Sample T_0). The progressive inclusion of nanoparticles during polymerization improves the resulting capacitance to 131.8 Fg^{-1} (sample T_2) as shown in Fig. 4.

Continuous incorporation of titanium dioxide (above 9.6 mg) during polymerization reduces the capacitance, due to the progressive aggregation of TiO_2 nanoparticles and segregation of semiconductor/conducting polymer matrix.

The comparison of GCD curves of PPy/TiO_2 (sample T_2) and $\text{PPy}/\text{SWCNT}/\text{TiO}_2$ (sample C_2) confirms that superior electrochemical properties are verified for $\text{PPy}/\text{SWCNT}/\text{TiO}_2$ composites, as shown in Fig. 5. If compared with the corresponding sample (T_1) we can observe that sample C_1 requires a $2\times$ longer time for charge–discharge process. As a result, the specific capacitance (sample C_1) reaches 153 Fg^{-1} while progressive inclusion of complex (sample C_2) results in the best electrochemical performance (282 Fg^{-1}).

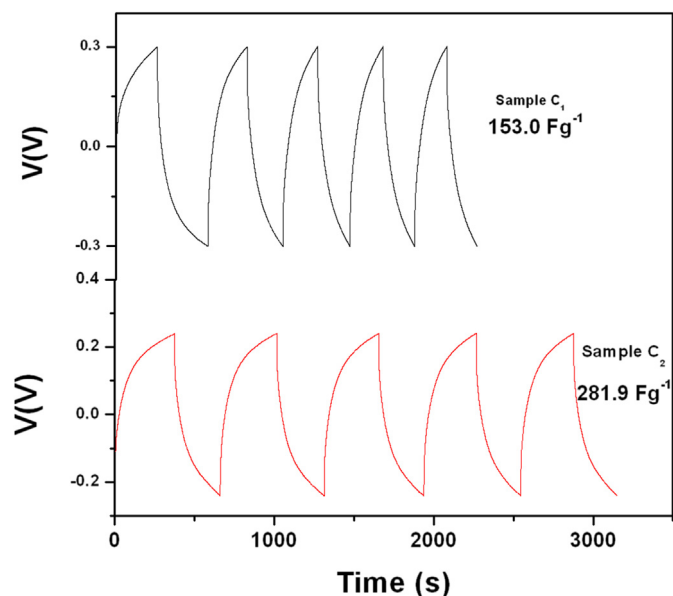


Fig. 5. GCD curves of composites at different relative concentration of $\text{SWCNT}/\text{TiO}_2$ complex/PPy (samples C_1 and C_2).

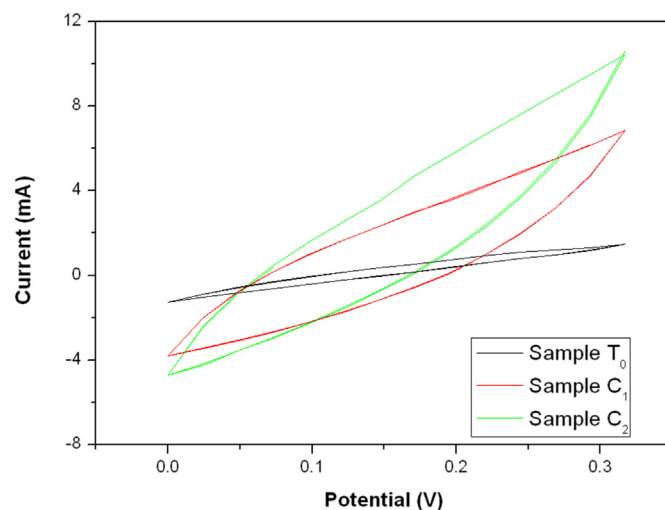


Fig. 6. CV curves (at scan rate of 10 mV s^{-1}) of composites at different relative concentration of $(\text{TiO}_2/\text{SWCNT})$ complex/PPy.

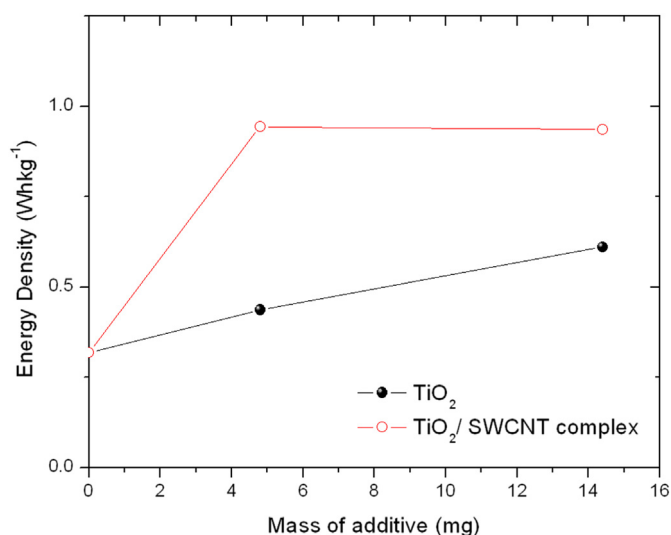


Fig. 7. Energy density of composite at different relative concentration of (TiO₂/SWCNT) complex/PPy.

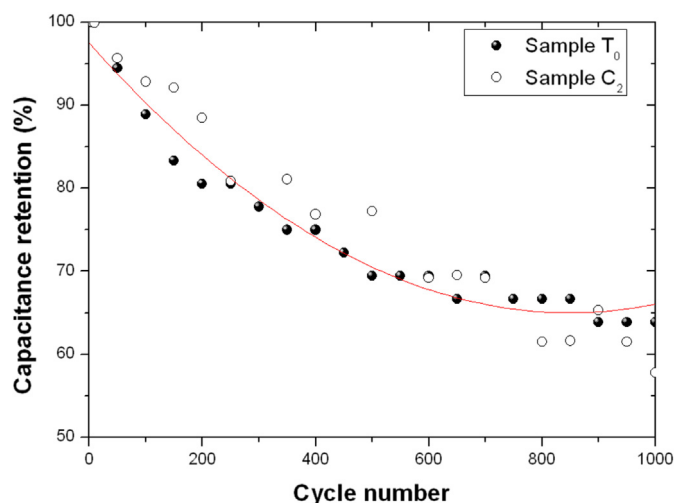


Fig. 8. Comparison of cycling performance of PPy and PPy/TiO₂/SWCNT composite (samples T₀ and C₂) at discharging current of 0.5 Ag⁻¹.

Fig. 6 shows overlaid CVs of composites of PPy/SWCNT/TiO₂ at different relative concentration of additives (samples T₀, C₁ and C₂). The behavior of resulting curves indicates that pseudocapacitance effects dominate in the overall response of devices, since Faradaic process is established during charge storage. The relation established between amount of additive (TiO₂/SWCNT complex) and area of corresponding CV curve is in agreement with results obtained for GCD technique, in an indication that progressive inclusion of complex improves the capacitance of resulting device.

The energy density of resulting devices is affected by incorporation of TiO₂ nanoparticles and TiO₂/SWCNT complex (as shown in Fig. 7) providing superior electrochemical response with incorporation of complexes. In spite of reasonable level of capacitance, a low specific energy density is verified for composites with

incorporation of neat titanium dioxide nanoparticles. On the other side, composites of polypyrrole/TiO₂/SWCNT (sample C₁) are characterized by energy density (E_{SC}) in order of 1 Wh kg⁻¹, as a result of strong interaction of carbon nanotubes and TiO₂ nanoparticles into polymeric templates.

Other important parameter for measurement of stability of supercapacitor is related with cycling performance of synthesized material. As we can see in Fig. 8, the capacitance retention of supercapacitor of neat polypyrrole (sample T₀) is compared with corresponding curve for ternary composite (sample C₂). The results indicate a reduction in the capacitance during initial test (200 cycles) and a gradual convergence of capacitance retention to 63.9% (1000 cycles of charge/discharge).

4. Conclusion

The association of titanium dioxide nanoparticles and SWCNT during chemical synthesis of hollow nanotubes of polypyrrole returns promising results for charge storage in organic electrodes. The specific capacitance of device is improved to 281.9 Fg⁻¹ as a result of superior electrical properties of polymeric composite. The improvement in the specific energy density and characterizes the composite of PPy/SWCNT/TiO₂ (sample C₂) as a potential candidate for development of new electrochemical devices with high performance for energy storage.

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